V.M.11 Lead Research and Development Activity for DOE's High Temperature, Low Relative Humidity Membrane Program (HTMWG) Year 1 Annual Report

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Contract Number: DE-FC36-06GO16028

Subcontractors:
- BekkTech LLC, Loveland, CO
- Scribner Associates, Inc., Southern Pines, NC

Project Start Date: April 1, 2006
Project End Date: March 31, 2009

Objectives

- Demonstrate conductivity of 0.07 S/cm, at 80% relative humidity (RH), at room temperature, using new polymeric electrolyte phosphotungstic acid (PTA) membranes.
- Demonstrate conductivity of >0.1 S/cm at 120°C and 1.5 kPa inlet water vapor partial pressure to the fuel cell stack.
- Standardize methodologies for in-plane and through-plane conductivity measurements.
- Provide High Temperature Membrane Working Group (HTMWG) members with standardized tests and methodologies.
- Organize HTMWG bi-annual meetings.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

(C) Electrode Performance

(D) Thermal, Air and Water Management

Technical Targets

FSEC will develop and evaluate new polymeric electrolyte PTA composite membranes to increase conductivity. FSEC will also develop standardized experimental methodologies to 1) measure conductivity (in-plane and through-plane), 2) characterize mechanical, mass transport, and surface properties of the membranes, and 3) predict durability of the membranes and their membrane electrode assemblies.

The membranes will meet the following DOE targets:

- A non-Nafion® membrane with a demonstrated conductivity of 0.07 S/cm at 80% RH at room temperature by the third quarter of year two.
- *A membrane with* a demonstrated conductivity of >0.1 S/cm at 120°C and 1.5 kPa water vapor partial pressure (50% RH measured at room temperature). This is a go/no-go decision point for the third quarter of year three.

Accomplishments

- Fabricated and tested FSEC-1 membrane (solved RH issue for fabrication).
- Determined optimum ranges of sulfonation for sulfonated poly(ether ether ketone) (SPEEK)/ sulfonated poly(ether ketone ketone) (SPEKK).
- Completed first conductivity test of SPEEK/SPEKK composite membranes (Year 1 milestone).
- Constructed membrane electrode assembly (MEA) fabrication equipment.
- Established baseline conductivity for commercial membranes using in-plane technique.
- Acquired preliminary Gurley numbers for gas diffusion layers.

- Developed and verified performance of primary components of prototype through-thickness membrane conductivity test system (MTS) (Year 1 milestone).
- Performed preliminary characterization of the through-thickness conductivity of Nafion® as a function of RH and temperature.
- Compared reported through-plane and in-plane conductivity data of Nafion®.
- Demonstrated feasibility of using Model 850C Compact Fuel Cell Test System for wet-dry gas mixing for rapid dew point and RH cycling.

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Introduction

Proton exchange membrane fuel cells (PEMFCs) have increasingly received worldwide attention due to their potential use in the hydrogen economy. Generally two regimes of PEMFC operation exist: the typical operating temperatures between 60 to 80°C and elevated temperatures higher than 100°C. The ability for current automotive radiators to reject heat is insufficient at continuous full power waste heat loads for 60 to 80°C fuel cell stack temperatures. Running the stack at 120ºC under full load would allow the use of radiators similar to those available in automobiles today. This has driven the need for development of high-temperature membranes and membrane electrode assemblies that could operate at temperatures of up to 120ºC, low RH and near atmospheric pressure.

The objective of the current project is to develop a fuel cell membrane material that meets the goals outlined by the DOE in the multi-year plan. Additional goals are: operation at elevated temperatures (up to 120°C) with a demonstrated conductivity of >0.1 S/cm at 120ºC and 1.5 kPa inlet water vapor partial pressure to the fuel cell stack (50% RH measured at room temperature). The material needs to operate over a range of operating conditions from -20 to 120ºC because conductivity at the lower temperature is necessary to achieve both quick start-up from cold temperatures and efficiency targets. Inlet water pressures of 25 kPa today are acceptable, but 1.5 kPa at the end of this five-year project is required. The membrane electrode assemblies fabricated from the membranes must meet durability targets in the aggressive environment of a fuel cell, i.e., the material must have good chemical stability and be resistant to oxidation by radicals produced in the cell during operation. They must also maintain adequate mechanical strength.

Approach

Our approach to preparing a membrane that will meet the requirements is two-fold. In Task 1, we are preparing Nafion®-based poly[perfluorosulfonic acid]-phosphotungstic acid composite membranes. In Task 2 we are developing a sulfonated poly(ether ketone ketone) or sulfonated poly(ether ether ketone) - phosphotungstic acid composite membrane.

Additionally, as the lead organization for the High Temperature Membrane program, we are working to standardize the methods used for making in-plane conductivity measurements, as well as developing a novel approach to through-plane measurements. These standardized methods will be used to perform conductivity measurements on membranes supplied by the working group members.

Results

During this first year, activity was conducted on both the independent high temperature membrane activity at FSEC and the coordination of the high temperature working group activity. In the independent FSEC work, the FSEC-1 membrane was fabricated and tested. This membrane was an 1,100 equivalent weight (EW) PFSA–Teflon®–phosphotungstic acid composite membrane. Initially, there was a problem with quality of the membranes that resulted from the high RH in Florida. This problem was resolved by constructing a drybox for membrane fabrication.

After verifying FSEC's ability to prepare membranes of acceptable quality, the first sample of a 750 EW polymer membrane was fabricated and initial testing performed. This membrane will undergo complete testing during Year 2 Q1.

Significant progress was made in the fabrication and evaluation of membranes fabricated with SPEEK and SPEKK. The first project milestone for the SPEEK/SPEKK membranes was met and a SPEEK membrane

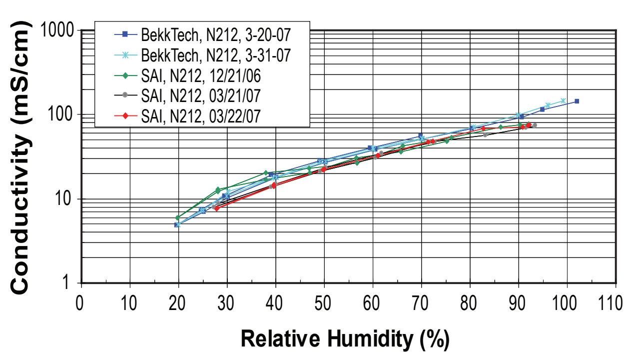

FIGURE 1. Comparison of In-Plane (BekkTech) to Through-Plane (Scribner) Conductivity

(analogous to the FSEC-1 series) was cesium treated and tested. While conductivity does not equal that of Nafion®, the preliminary results are encouraging. The optimum degree of sulfonation was determined and cross-linking has resulted in an insoluble polymer.

In-plane conductivity testing of commercial samples was completed and the results, Figure 1, shared with the group. This information will be used for comparison to the membranes from the working group members.

A major objective of this first year was to develop a prototype test system for measurement of the through-thickness resistance of proton exchange membranes (PEMs). To this end, the primary components of a prototype through-thickness MTS were developed and its performance verified. This achieved the second milestone for Year 1. Evaluation of the first generation of the prototype MTS indicated stable and repeatable control of the gas and membrane specimen temperature and RH to better than ±0.5°C and ±2% RH for RH between 20% and 90%, respectively, at 80°C.

The data obtained by the in-plane method was compared to that obtained using the through-plane approach, Figure 2. In general, the Scribner's through-thickness conductivity of Nafion® NRE-212 at 80°C was slightly less than the in-plane data of BekkTech. It is uncertain if discrepancy in the values are real (*i.e.*, there is an difference in the intrinsic conductivity in the two different orientations) or if there is an artifact in either or both sets of data. Additional analysis will be necessary to ascertain the origin of the discrepancy.

Although differences in the absolute values exist between Scribner's and BekkTech's data, some features are common to both. The relationship between conductivity and RH is observed for both in-plane and through-plane measurements. Also, the hysteresis in the conductivity with RH cycling reported by BekkTech is reproduced in Scribner's data.

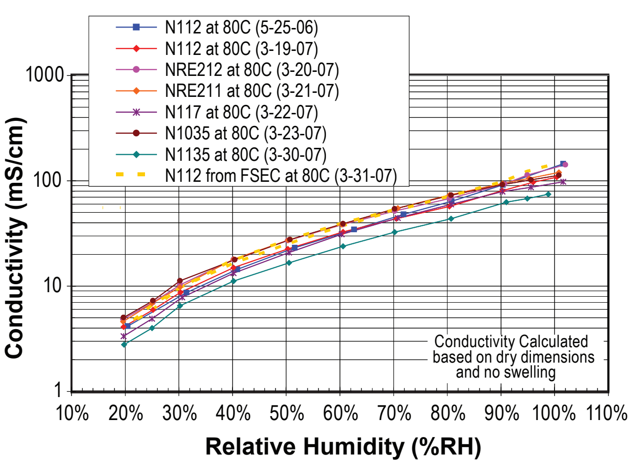

FIGURE 2. Four Electrode Conductivity of Nafion® at 80°C

Conclusions and Future Directions

Work during this first contract year has validated FSEC's ability to fabricate membranes of acceptable quality, and established the groundwork for testing membranes from the working group members. Baseline measurements of standards are available for comparison to data from new materials. Additionally, a new method for conducting through-plane measurements has been developed. During this upcoming year, work will continue on developing a new low EW monomer as well as continuing the work on SPEEK and SPEKK. We are also prepared to begin testing samples from the working group. The following bullets contain a summary of the tasks to be accomplished.

- Fabricate and test new membrane formulations with low EW PFSA and SPEEK/SPEKK.
- Perform conductivity test on these membranes, as well as the membranes supplied by the Task 1 members (Year 2 Q4 Milestone).
- Perform water balance analysis to resolve source of discrepancy in dew point and RH measurements at 120°C, 230 kPa.
- Characterize Nafion® through-thickness conductivity as a function of RH at 30°C, 80°C and 120°C (Year 2 Q2 Milestone).

FY 2007 Publications/Presentations

1. K.R. Cooper "Through-Plane Conductivity Test System for the High Temperature, Low Relative Humidity Membrane Program" Advances in Materials for Proton Exchange Membrane Fuel Cell Systems 2007, Pacific Grove, CA, February 18-21, 2007.

2. V. Mittal, J. M. Fenton. "Membrane Degradation Mechanisms in PEM Fuel Cells," December 4, 2006, Presentation to 3M Fuel Cells Group, Minneapolis, MN.

3. J. M. Fenton. "High Temperature, Low Relative Humidity Membrane Working Group," An invited Presentation to the Fuel Cell Technical Team at The United States Council for Automotive Research (USCAR) in Detroit Michigan, December 6, 2006. Presentation given on behalf of the U.S. Department of Energy.

4. V. Mittal, J.M. Fenton, H.R. Kunz. "Membrane Degradation Mechanisms in Polymer Electrolyte Membrane Fuel Cells," Fuel Cells Durability and Performance, Real World Solutions to the Most Significant Challenge Facing Fuel Cells Commercialization. December 6-8 2006, Miami Beach, FL.

5. J.M. Fenton. "Polymer Electrolyte Fuel Cells…. for the Rest of Us," Invited Plenary Presentation. The Electrochemical Society Meeting, Cancun, Mexico, Sunday, 6:30 to 7:30 pm, Oct. 29, 2006.

6. J.M. Fenton, H. Xu; H.R. Kunz "Improvement of PEM Fuel Cell Performance Using Low Equivalent Weight Ionomers and Pt-Co/C in the Cathode." The

Electrochemical Society Meeting, Cancun, Mexico, Oct. 29-Nov. 3, 2006. Electrochemical Society Extended Abstracts 602, Abstract Number 530.

7. H. Xu, J.M. Fenton, M.Wu, Y. Liu V. Mittal, F. Kassim, B. Vieth, L. Bonville, H.R. Kunz. "MEA Durability Test of PEM Fuel Cells at 100°C and 25% RH." The Electrochemical Society Meeting, Cancun, Mexico, Oct. 29-Nov. 3, 2006. Electrochemical Society Extended Abstracts 602, Abstract Number 487.

8. V. Mittal, J.M. Fenton, H.R. Kunz. "Membrane Degradation Mechanisms in PEMFCs" The Electrochemical Society Meeting, Cancun, Mexico, Oct. 29-Nov. 3, 2006. Electrochemical Society Extended Abstracts 602, Abstract Number 448.

9. R. Zaffou, J.M. Fenton, H.R. Kunz. "Temperature-Driven Water Transport in Polymer Electrolyte Fuel Cells." The Electrochemical Society Meeting, Cancun, Mexico, Oct. 29-Nov. 3, 2006. Electrochemical Society Extended Abstracts 602, Abstract Number 423.